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<p>(21) International Application Number: PCT/GB96/00300 (22) International Filing Date: 5 February 1996 (05.02.96) (30) Priority Data: 9502341.2 7 February 1995 (07.02.95) GB (71) Applicants (for all designated States except US): ILFORD A.G. [CH/CH]; Industriestrasse 15, CH-1701 Fribourg (CH). MATTHEWS, Richard, Nordan [GB/GB]; Ilford Limited, Town Lane, Mobberley, Knutsford, Cheshire WA16 7JL (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): BAETTIG, Kurt [CH/CH]; Sur le Village, CH-1724 Praroman (CH). JAN, Gerald [CH/CH]; Route du Bugnon 27, CH-1752 Villars-sur-Glâne (CH). (74) Agent: MATTHEWS, Richard, Nordan; Ilford Limited, Town Lane, Mobberley, Knutsford, Cheshire WA16 7JL (GB).</p>		<p>(81) Designated States: CA, GB, JP, US, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: DYES FOR INK JET PRINTING (57) Abstract There is described a new magenta azo dye which can be used in an aqueous composition in an ink jet printing process.</p>		

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Dyes for ink jet printing

Field of the invention

The present invention relates to dyes and aqueous ink compositions comprising these dyes for ink jet printing processes.

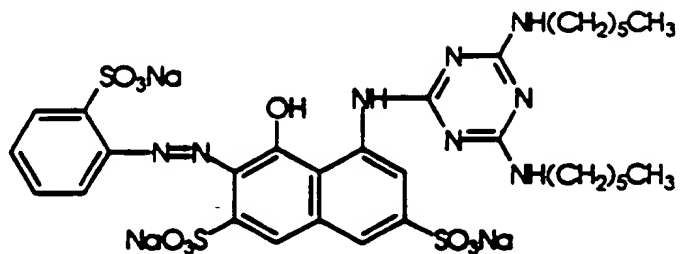
Ink jet printing systems generally are of two types: continuous stream and drop-on-demand. In continuous stream ink jet systems, ink is emitted in a continuous stream under pressure through an orifice or nozzle. The stream is perturbed, causing it to break up into droplets at a fixed distance from the orifice. At the break up point, the droplets are charged in accordance with digital data signals and passed through an electrostatic field which adjusts the trajectory of each droplet in order to direct it to a waste ink collecting vessel (e.g. for recirculation) or a specific location on a recording medium. In drop-on-demand systems, a droplet is expelled from an orifice to a position on a recording medium in accordance with digital data signals. A droplet is not formed or expelled unless it is to be placed on the recording medium.

The most important part of an ink used in ink jet printing are the dyes. Although a number of dyes have been proposed none has been produced which meets all the requirements of a modern printing process.

Background of the invention

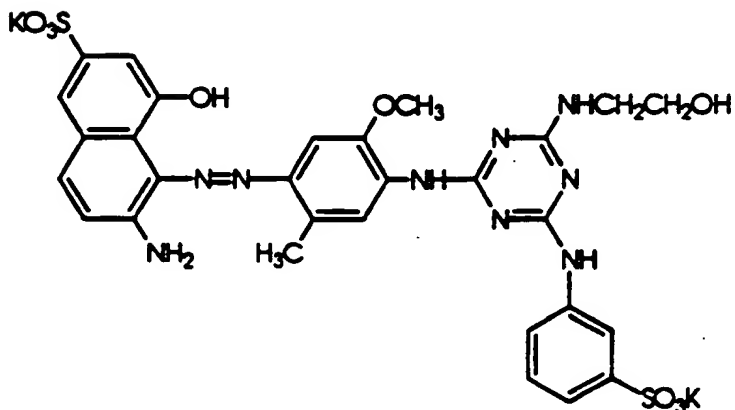
Reactive dyes with incorporated 1,3,5-triazine structural elements are common in textile printing and have also been proposed for ink jet printing. Such dyes are for several reasons in general not too well suited for this application. The reactive groups are not very stable over prolonged periods in aqueous solutions. Dyes containing such reactive groups are moreover, due to their potential health risk, less suitable for handling in a non industrial environment. Non reactive dyes of this kind have been described in USP 4,771,129

(K. Hideo) and USP 4'777'248 (D. Greenwood). In particular dyes of the following structural formulas have been described:



USP 4'771'129 (dye 5)

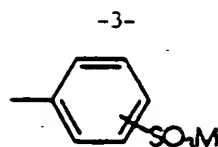
(1)



USP 4'777'248 (dye 1)

(2)

In some of these dyes particularly enhanced water-solubility has been claimed to be due to the introduction of elements of the following structure



(3)

and in some cases water solubility seems still to be improved by introduction of elements of the structure



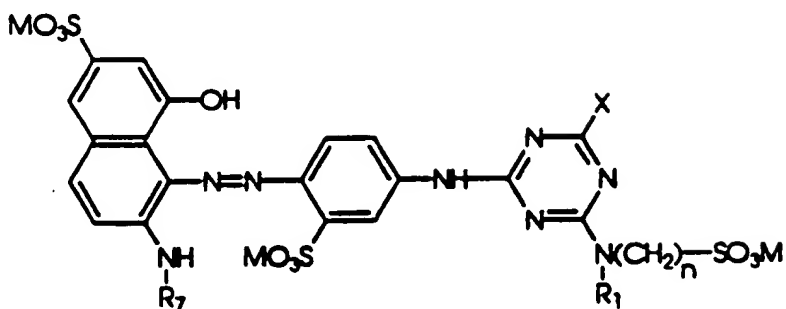
(USP 4'777'248) into the triazine part of the dye.

These dyes are however still inadequate when used in aqueous inks of modern ink jet printers. In particular printers of the continuous-stream type are highly demanding as far as physical properties of the inks are concerned. Particularly critical are storage stability of the inks without forming degradation products prone to clog the nozzles of the printer. Printers are today able to print images of high density rapidly. Therefore highly concentrated inks are needed in order to avoid the jetting of high water volumes onto the receiving layer. These high concentrations should ideally, for environmental reasons, be achieved without the use of organic cosolvents. Such inks can only be prepared with dyes having a particularly high water solubility.

Dyes of the above mentioned structures which are the state of the art, are in general not soluble enough to satisfy the required demanding conditions. It is the aim of this invention to provide dyes with the required high water solubility.

Description of the invention

This invention relates to azo dyes of the formula (4)



(4)

wherein:

R_1 is selected from hydrogen or an aliphatic radical having from 1 to 6 C atoms:

n is 2, 3 or 4;

X is NR_3R_4 where

R_3 and R_4 are independently selected from hydrogen, alkyl from 1 to 6 C atoms, C2 to C6 substituted alkyl where the substituents are selected from OH, OCH_3 , COOM, SO_3M ; aralkyl; unsubstituted aryl or an aryl substituted by COOM or SO_3M ;

R_3 and R_4 may form a ring without or with inclusion of a hetero atom;

or

X is SR_5 in which R_5 is alkyl from 1 to 6 C atoms, C2 to C6 substituted alkyl where the substituents are selected from OH, OCH_3 , COOM, SO_3M ;

or

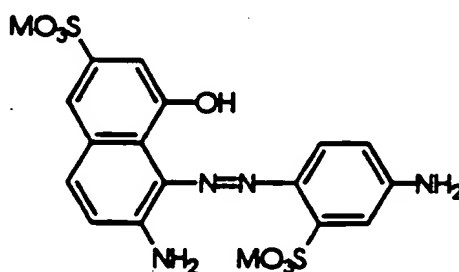
- X is OR_6 in which R_6 is hydrogen or an aliphatic radical having from 1 to 6 C atoms;
- R_7 is hydrogen, alkyl of 1 to 6 C atoms, C2 to C6 substituted alkyl where the substituents are selected from CN, COOM, OH, COOCH₃, COOCH₂CH₃, COCH₃; unsubstituted aryl or aryl substituted by CH₃, halogen;
- M is hydrogen, a metal atom, an ammonium or ammonium substituted with alkyl, alkoxyalkyl and hydroxyalkyl each having 1 to 12 C atoms.

The azo dyes of the present invention comprise no reactive groups. They are of particular use in inks used for ink-jet printing because of their high water solubility.

Dye Synthesis

One method of preparing dyes of the present invention is by

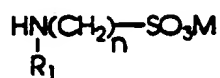
- (1) Reacting the known (USP 3'787'215) monoazo compound of formula (5)



(5)

with cyanuric chloride under conditions such that one chlorine atom of the triazine is displaced by the monoazo compound of formula (5) then

- (ii) reacting the mono-substituted dichloro-triazine with a compound of formula (6)



(6)

under conditions such that a second atom of chlorine is displaced by the compound of formula (6) and

- (iii) reacting finally the di-substituted triazine with a compound XH under conditions that the third chlorine atom is displaced by X.

Where X is a compound of formula (6), the second and third chlorine atoms of the triazine nucleus may be replaced simultaneously.

The present invention is illustrated by the following example.

Example 1

Preparation of the compound No.100 (Na-salt)

step 1

48.3 g (0.1 mol) monoazo compound (5) was added to water (600 ml) and the pH adjusted to 8 by addition of 30 % aq. sodium hydroxide solution.

A solution of cyanuric chloride (20.3 g, 0.11 mol) in ethyl acetate (100 ml) was added maintaining the pH at 7 to 8 and the temperature at 15 - 20° C. After 30 minutes a solution of 2-aminoethane-sulfonic acid, sodium salt (17.8 g, 0.12 mol) in water (120 ml) was added to the reaction mixture while maintaining the pH at 7 - 7.5 and the temperature at 30° C. After 30 minutes the reac-

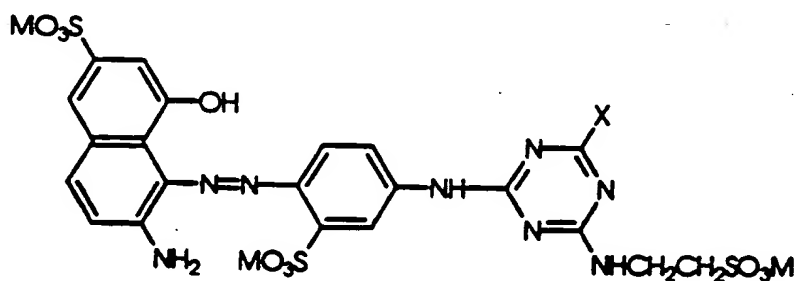
tion mixture was heated to 50° C and stirred for 1 hour at this temperature, cooled to room temperature and then the product was filtered.

step 2

The wet product (200 g) from step 1 was added to a solution of 1-methyl-2-pyrrolidinone (200 ml) and 2-(methylamino)ethanol (18 g, 0.24 mol). The reaction mixture was heated to 90° C for 3 hours and cooled to room temperature. A solution of 12 g of sodium acetate in ethanol (400 ml) was added to the reaction mixture. The solid was collected by filtration, washed with ethanol (300 ml), dried in vacuum at 60° C to yield the magenta dye (64 g) of formula No. 100.

In an analogous manner using appropriate starting materials the dyes described in Tables 1 and 2 can be obtained.

The dyes of general formula

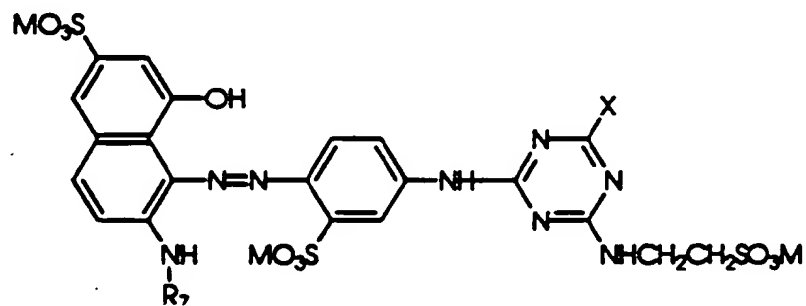


were made wherein the substituents are:

Compound No.	X	M	λ max (nm) in H ₂ O
100	N(CH ₃)CH ₂ CH ₂ OH	Na	519
101	N(CH ₂ CH ₂ OH) ₂	Na	518
102	NHCH ₂ CH ₂ SO ₃ Na	Na	516
103	S(CH ₂) ₃ SO ₃ K	K	518
104	SCH ₂ CH ₂ OH	Na	516
105	OH	Na	516
106	SCH ₂ COOK	K	517
107	OCH ₂ CH ₃	Na	515

Table 1

The dyes of general formula



were made wherein the substituents are:

Compound No.	R7	X	M	λ_{max} (nm) in H ₂ O
200	CH ₂ CH ₂ CN	N(CH ₃)CH ₂ CH ₂ OH	Na	528
201	CH ₂ CH ₂ CN	SCH ₂ CH ₂ OH	Na	526

Table 2Example 2

The dyes of the present invention are specially adapted for the preparation of inks. Inks for ink jet printing are well known. These inks consist in essence of a liquid vehicle dissolved therein a dye. The liquid vehicle of the inks employed for the printing consists in general of water or a mixture of water and a miscible organic solvent such as C1-C4 alkanols, alkylene glycols such as di(propylene glycol), di(ethylene glycol), polyols such as 1,5-pentanediol, glycerol, 1,2,6-trihydroxyhexane, nitrogen-containing solvents such as 2-pyrrolidinone, N-methyl-2-pyrrolidinone, 1-(2-hydroxyethyl)-2-pyrrolidinone, 1,3-dimethyl-2-imidazolidinone, 1,1,3,3-tetramethylurea or sulfur containing solvents such as organosulfoxides, sulfolane and the like.

The non water parts of the printing ink generally serve as humefactant, cosolvent, viscosity regulating agent, ink penetration additive, levelling agent or drying agent.

In addition aqueous inks may contain miscellaneous known additives like viscosity modifiers, such as cellulose derivatives and other water-soluble resins, various kinds of surfactants, surface tension modifiers, optical brighteners, UV absorbers, light stabilisers, biocides and pH conditioners, such as buffers.

Inks for use in ink jet recording of the type based on continuous-stream usually contain an inorganic salt as electrolyte, such as sodium/ammonium/lithium halogenides or sulphate.

This description of inks is for illustration only and is not to be considered as limiting the invention.

The present invention in so far as it relates to inks is further illustrated with reference to the following examples in which all parts and percentages are by weight.

Inks were prepared, using the dyes 100 to 102, as described above, according to the following recipe:

dye	6 parts
glycerol	20 parts
water	74 parts

The inks were prepared by dissolving the ingredients and filtering the solution under pressure through a Millipore filter (0.5 micron).

The inks were tested and shown to satisfy all the requirements specifying a usable ink. In particular they were shown to meet the following criteria:

- (1) Physical properties of the ink, such as viscosity, conductivity and surface tension, are each within a defined range.
- (2) All dyes have good solubility in the ink medium to give solutions having good stability which do not plug the fine ejecting orifices.
- (3) The recording agent gives images of sufficient optical density.
- (4) The ink does not change physical properties or deposit solid matter during storage.

- (5) Printing can be performed without a restriction on the nature of substrate.
- (6) The ink exhibits a high rate of fixation.
- (7) The ink gives images of good resistance to water, light and abrasion.

Example 3

The solubilities of the dyes according to the invention were determined as follows:

An excess of dye was heated at 50° C in water with stirring for one hour. The mixture was then cooled down to 20° C and filtered, and the dye content of the clear solution was determined spectroscopically. The results obtained are shown in table 3

Dye No	Solubility (in g per 100 ml)
100	35
101	32
102	26
dye 1	20
dye 5	15

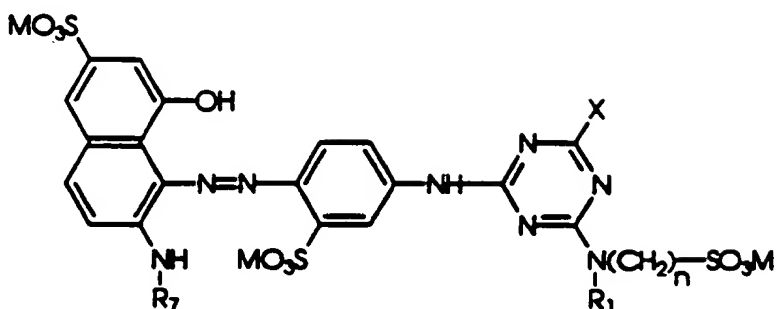
Table 3

The dyes 1 and 5 are known from USP 4'777'248 and USP 4'771'129 as heretofore set forth.

The results in table 3 show the significantly higher solubility of the dyes according to the invention compared to dyes of the prior art.

CLAIMS:

1. An azo dye of formula (4)



(4)

wherein

R_1 is selected from hydrogen or an aliphatic radical having from 1 to 6 C atoms;

n is 2, 3 or 4;

X is NR_3R_4 where

R_3 and R_4 are independently selected from hydrogen, alkyl from 1 to 6 C atoms, C2 to C6 substituted alkyl where the substituents are selected from OH, OCH_3 , $COOM$, SO_3M ; aralkyl; unsubstituted aryl or an aryl substituted by $COOM$ or SO_3M ;

R_3 and R_4 form a ring without or with inclusion of a hetero atom;

or

X is SR_5 in which R_5 is alkyl from 1 to 6 C atoms, C2 to C6 substituted alkyl where the substituents are selected from OH, OCH_3 , $COOM$, SO_3M ;

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or

- X is OR_6 in which R_6 is hydrogen or an aliphatic radical having from 1 to 6 C atoms;
- R_7 is hydrogen, alkyl of 1 to 6 C atoms, C2 to C6 substituted alkyl where the substituents are selected from CN, COOM, OH, COOCH₃, COOCH₂CH₃, COCH₃; unsubstituted aryl or aryl substituted by CH₃, halogen;
- M is hydrogen, a metal atom, an ammonium or ammonium substituted with alkyl, alkoxyalkyl and hydroxyalkyl each having 1 to 12 C atoms.

2. An azo dye according to claim 1 where

R_1 is hydrogen and where

X, n, R_3 to R_7 and M are as set forth in claim 1.

3. An azo dye according to claim 2 where

n is 2 or 3;

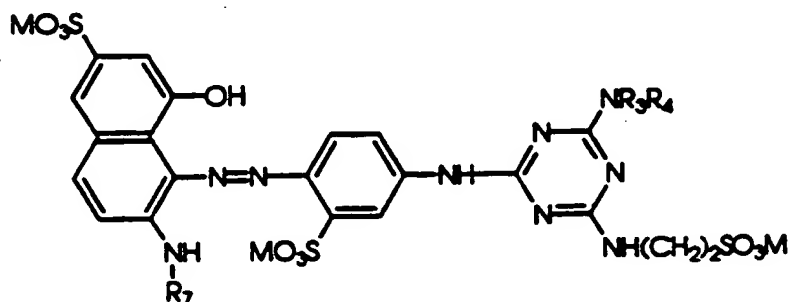
R_3, R_4 are independently selected from hydrogen, C1 to C6 alkyl, C2 to C6 substituted alkyl where the substituents are selected from OH, OCH₃, COOM, SO₃M or R_5, R_6 form a 5- or 6-membered ring without or with inclusion of a hetero atom;

R_5 is a C1 to C4 substituted alkyl where the substituents are selected from OH, COOM or SO₃M;

R_6 is hydrogen, CH₃ or CH₂CH₃;

R_7, M are as set forth in claim 1.

4. An azo compound according to claim 3 where
 R_7 is selected from hydrogen, C1 to C3 alkyl or C2 or C3 substituted alkyl where the substituents are CN or COOM.
5. An azo dye according to claim 4 where
 R_5 is $\text{CH}_2\text{CH}_2\text{OH}$, CH_2COOM or $(\text{CH}_2)_3\text{SO}_3\text{M}$;
 R_6 is hydrogen;
 M is hydrogen, alkali metal atom, ammonium or ammonium substituted with C1 to C2 alkyl or with $\text{CH}_2\text{CH}_2\text{OH}$.
6. An azo dye according to formula (7)



(7)

where

- R_3, R_4 are independently selected from hydrogen or C2 to C3 substituted alkyl where the substituents are selected from OH, COOM or SO_3M ;
- R_7 is hydrogen, $\text{CH}_2\text{CH}_2\text{CN}$ or $\text{CH}_2\text{CH}_2\text{COOM}$ and
- M is hydrogen, alkali metal or ammonium ion.
7. An ink comprising a dye or a mixture of dyes as described in anyone of claims 1 to 6.

8. An ink which contains in addition to a dye or dyes as claimed in any-one of claims 1 to 6 one or more other dyes.

INTERNATIONAL SEARCH REPORT

 b) Application No
 PCT/GB 96/00300

 A. CLASSIFICATION OF SUBJECT MATTER
 IPC 6 C09B43/16 C09D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

 Minimum documentation searched (classification system followed by classification symbols)
 IPC 6 C09B C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Content of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 187 520 (ICI PLC) 16 July 1986 see page 4, line 24 - line 31; example 4 & US,A,4 777 248 (D.GREENWOOD) cited in the application ---	1-8
A	EP,A,0 194 885 (TAOKA CHEMICAL CO LTD ;SUMITOMO CHEMICAL CO (JP)) 17 September 1986 cited in the application see page 6, line 3 - line 6; claims 1,2 ---	1-8
A	DE,A,22 58 837 (AGFA GEVAERT AG) 12 June 1974 see compounds 1-3; claim ---	1-8
A	US,A,3 142 669 (J.F.FEEMAN) 28 July 1964 see column 3, line 58 - column 4, line 7; example 32 -----	1-6

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

23 May 1996

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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DE-A-2258837	12-06-74	FR-A,B 2208791 GB-A- 1455877 JP-A- 49089534 SE-B- 395466 US-A- 3889271	28-06-74 17-11-76 27-08-74 15-08-77 10-06-75
US-A-3142669	28-07-64	NONE	